

PATENT SPECIFICATION

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DRAWINGS ATTACHED

- (21) Application No. 39371/68 (22) Filed 16 Aug. 1968
(31) Convention Application No. 661 459 (32) Filed 17 Aug. 1967 in
(33) United States of America (US)
(45) Complete Specification published 7 Oct. 1970
(51) International Classification B 32 b 5/18

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BSN 177 17X 17Y 188 191 20Y 214 22X 22Y 252Y 254Y
255Y 344 348 349 350 351 353 354 355 35X 35Y
42Y 543 555 55X 57X 591 598 60Y 620 641 654
656 660 663 666 669 66Y 670 674 679
682 687 69X 69Y 706 707 763 766 769 774 781 787
788 789 793



(54) SUEDE-LIKE PLASTICS MATERIAL AND METHOD OF
MAKING SAME

PATENTS ACT 1949

SPECIFICATION NO. 1,208,056

The following amendments were allowed under Section 29 on 7 September 1971:-

Page 1, *delete* lines 54 and 55 *insert* 'appearance to both surfaces which have been split open by tensile rupture. In a preferred embodi-

Page 1, *delete* lines 57 to 59 *insert* 'cellular structure.'

Page 2, lines 34 and 35, *delete* 'one or'

Page 6, *delete* lines 64 and 65, page 7, lines 22 and 23, *insert* 'appearance to both surfaces which have been split open by tensile rupture.'

Page 6, *delete* line 120 *insert* 'to both surfaces which have been split open by tensile rupture.'

THE PATENT OFFICE
1 October 1971

R 4904/10

PATENTS ACT 1949

SPECIFICATION NO. 1,208,056

The following corrections were allowed under Section 76 on 18 August 1971:-

Page 1, line 1, for 'INCORPORATED' read 'INC.'

THE PATENT OFFICE
1 October 1971

R 4904/19

... which also requires an abrasion operation is described in U.S. Patent Speci-
and the amount and type of plasticiser employed. Other methods include without limitation the use of physical methods such as

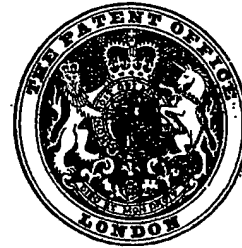
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(54) SUEDE-LIKE PLASTICS MATERIAL AND METHOD OF MAKING SAME

(71) We, PANDEL INCORPORATED, a Corporation organized and existing under the laws of the State of Massachusetts, United States of America, of 246 Market Street, Lowell, State of Massachusetts, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of sheet materials having a suede-like surface appearance.

Normally the surface of plastics sheeting such as vinyl chloride resin sheet is smooth and shiny in appearance. It is often desirable to prepare plastics surfaces which have a different appearance, feel or texture for use, for example, as a decorative covering or for utilitarian purposes. It is particularly desirable to prepare a soft flexible plastics-coated sheet material which has the feel and appearance of a more expensive suede-like material such as leather. Previous attempts to obtain such a suede-like material have not been wholly successful. Some methods have been directed toward separate or additional treatments of the surface of a plastics material to obtain the desired appearance. This has often resulted in a product of less than acceptable appearance, while any additional treatment has resulted in a more expensive operation than is commercially acceptable. For example, U.S. Patent Specification No. 3,041,193 describes a method of making a suede-like plastics-coated sheet material by preparing a cellular polyvinyl coating on a fabric sheet and then abrading the exposed surface of the cellular layer to produce a suede-like finish. Another technique which also requires an abrasion operation is described in U.S. Patent Specification No. 3,312,586.

We have now found that a sheet material having a suede-like surface appearance can be prepared by forming a laminate comprising two outer layers forming backing sheets and two intermediate layers of thermoplastic resin, at least one of the intermediate layers having a cellular structure, and stripping apart the two backing sheets along the bonding plane between the two intermediate layers whereby to rupture the cells at the surface of the cellular layer and to impart a suede-like surface appearance to the intermediate layer or layers of cellular structure. In a preferred embodiment both of the intermediate layers have a cellular structure and suede-like surfaces are imparted to both of the intermediate layers to each of which a backing sheet is laminated.

In general, the relative thicknesses of the two intermediate layers may be from 1:10 to 10:1 and preferably from 5:1 to 1:5.

The stripping apart of the backing sheets along the bonding plane between the two intermediate layers causes rupture of the cells at the surface of the cellular layer across the entire planar surface of the cellular layer and imparts an irregular or undulating natural suede-like surface to the product. This rupture is brought about as the result of a tensile gradient or a plane of tensile discontinuity which occurs between the surfaces of the first and second intermediate layers. The tensile gradient or discontinuity between the intermediate layers may be created by a number of methods including for example, degree of expansion, variation in the resin formulation and composition of the intermediate resin layers such as the variation of silica content, the type and molecular weight of the resin, and the amount and type of plasticiser employed. Other methods include without limitation the use of physical methods such as employing a temperature gradient across the

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SEE CORRECTION SLIP ATTACHED

laminated layers and varying the temperatures at which the lamination and/or delamination occurs, for example 250° to 450°F. Alternatively, a backing sheet is coated with a thermoplastic resin adhesive and is applied to a cellular layer on a second backing sheet. The adhesive chosen is one with sufficient cohesive strength to remove the top of the cellular layer upon delamination thereby providing the open-celled suede-like structure.

The sheet materials which are produced in accordance with the invention are composed of a sheet material having a cellular plastics coating thereon, the surface of the coating being characterised by an undulating or irregular surface which is generally uniformly composed of ruptured open cells and which presents a suede appearance to the surface. The material is flexible and has a soft hand. The exposed cell edges are rough and irregular and therefore provide a fibre-like characteristic similar to leather. The method of the invention permits a more natural undulating surface effect to be obtained since the stripping operation unlike a synthetic cutting operation or an abrasion operation provides a random irregular surface which may vary in thickness from a plane surface by, for example, from one to five mils. This is to be contrasted with an abrasion operation for example, wherein an abrading wire wheel gives a generally level regular surface across the entire fabric and destroys and reduces a portion of the surface in the operation. In our method, one or both surfaces which have been split open by tensile rupture have the desirable suede-like surface. By varying the temperature at which controlled delamination occurs, the amount of short fibres present and surface appearance of our material may be varied. Where a lower temperature of delamination is employed there is a greater tendency for the resin surfaces to form a fibrous surface, that is the resin tends to stretch more before breaking apart from the plane of tensile discontinuity or the bonding plane between the first and second sheet materials. At higher temperatures, there is usually less tendency for resin fibres to be pulled out in length, since the thermoplastic fibres tend to break quickly and, therefore, form short fibre lengths on the surface thereby giving a different appearance to the sheet material surface. Of course, the selection of the particular temperature or temperature range to use in the stripping operation depends upon the type of surface desired and upon the character of the resin and formulation employed.

One preferred method of preparing the material is to employ a first and second backing sheet material both of which are provided with a blowable plastics layer of different thicknesses, so that the formation of cellular layers from the blowable plastics layers and the subsequent controlled delamination, results

in the formation of sheet materials having surfaces of a suede-like appearance.

The term "tensile ruptured", as used herein is intended to refer to the cleavage of the cells at the weakest structural point to form ragged-edged, irregularly-shaped, open cells.

The invention will be described in more detail by reference to the accompanying drawings in which:

Figure 1 is a schematic illustration of one method of preparing a resin coated fabric having a suede-like surface in accordance with the invention.

Figure 2 illustrates cross-sections of enlarged fragmentary materials at various steps of the process illustrated by Figure 1.

Figure 3 is a schematic illustration of another method of preparing suede-like materials in accordance with the invention by the use of calendered resin sheets.

Figure 4 shows cross-sections of enlarged fragmentary materials as prepared by the method illustrated by Figure 3.

Figure 5 is an enlarged photographic view of the surface of a suede-like material prepared in accordance with the invention; and

Figure 6 is another enlarged photographic view of the surface of a suede-like material prepared in accordance with the invention.

A cellular vinyl chloride resin coated backing sheet or fabric having a suede-like cellular surface may be prepared by the use of resin formulations such as those set forth in Tables 1 and 2, hereafter, by the process illustrated by Figures 1 and 2, while a process employing calendered sheets of vinyl chloride resin is illustrated more particularly by Figures 3 and 4. Referring to Figure 1, a backing sheet of a thin inexpensive casting type paper 12 has a plastisol layer 18 cast onto the surface at a thickness of approximately one or two to ten mils, for example three to six mils. The vinyl chloride resin plastisol layer 18 is cast coated onto the surface from a source 14 by the use of a doctor blade 16 or other suitable coating technique. A typical plastisol formulation is set forth in Table 1 and is composed primarily of a low or medium molecular weight resin with an excess of plasticiser and is compounded to exhibit low hot film strength. The backing sheet 12 with the thin plastisol coating 18 is then passed through an oven 20 and heated to a temperature sufficient to gel and/or blow the vinyl chloride resin; typically, a temperature of 255° to 350°F, e.g. 300°F. is used. The dwell time in the oven is adjusted to provide a substantially tack-free coating surface on the gelled layer 18. After emerging from oven 20, another vinyl chloride resin plastisol formulation, such as that set forth in Table II, is cast coated from a source 22 by a doctor blade 24 to form a relatively thick layer 26 on the surface of the gelled vinyl chloride layer 18. The plastisol layer 26 is cast in a thickness of from 2 or 5 to

50 mils, preferably 10 to 30 mils, and has been compounded employing a high molecular weight polymer with lower plasticiser levels so as to have a higher hot film strength than layer 18. This formulation is selected to provide a coated layer having a natural suede-like appearance.

TABLE I

Ingredients	Parts by Weight
Low molecular weight polyvinyl chloride resin (EXON 605) ¹	50
Diluent resin (PLIOVIC M-70) ²	50
Filler (calcium carbonate)	15
Plasticiser	
a) Monomeric } nonyl octyl decyl adipate	12.0
} diisooctyl phthalate	44.0
b) Polymeric (SANTICIZER 845) ³ (containing isooctyl epoxy tallate)	4.0
Blowing agent (Kempore 200) ⁴ azodicarbonamide	1.75
Stabilizer (Actofoam-R-3) ⁵ mixture of zinc and potassium fatty acid salts in dioctylphthalate	0.75
TOTAL	177.50

1. A trademark of Firestone
2. A trademark of Goodyear
3. A trademark of Monsanto
4. and 5. Trademarks of National Polychemicals, Inc.

TABLE II

Ingredients		Parts by weight
Vinylchloride resin — dispersion		
grade (GEON 121) ¹		37.0
(GEON 222) ²		17.0
(PLIOVIC WO) ³		9.0
Diluent resin (PLIOVIC M—70) ⁴		35.0
Plasticiser		
a) monomeric	nonyl octyl phthalate	12.0
	Butyl dioctyl phthalate	10.0
	diisooctyl phthalate	29.0
b) polymeric (SANTICIZER 845) ⁵		3.0
blowing agent (KEMPORE 200) ⁶		
azodicarbonamide Stabilizer — activator (ACTOFOAM R—3) ⁷		2.0
TOTAL		154.0

1. and 2. A trademark of Goodrich

3. A trademark of Goodyear

4. A trademark of Goodyear

5. A trademark of Monsanto

6. and 7. Trademarks of National Polychemicals, Inc.

5 Backing sheet 12 with gel layer 18 and
 10 plastisol layer 26 is then passed to a hot air
 oven 28 wherein the layer 26 is heated to a
 temperature, as in oven 20, that is sufficient
 to gel the plastisol. The temperature of oven
 28 is typically from 300° to 400°F. Of course,
 the vinyl chloride resin layer 26 may be the
 same colour as layer 18 or may be a different
 15 colour to provide any desired contrast. The
 same resins or plasticisers may be employed
 in both layers but formulations with different
 properties are preferably employed. Where
 similar formulations are used then a tempera-
 20 ture gradient may be used to provide strip-
 able layers.

The gelling time in oven 28 should not be
 sufficient to provide a tack-free surface to
 layer 26. Layer 18 is normally gelled to a
 20 tack-free surface coating so that there is a
 reduction of migration of the layer 26 into
 layer 18 which may blur the plane of tensile

discontinuity and affect the controlled delam-
 ination which is desired. However, the top
 surface of layer 26 should be slightly tacky 25
 after emerging from oven 28. A backing sheet
 30 of fabric such as a woven cotton or non-
 woven material is then placed on the top sur-
 face of the tacky layer 26 and pressed into
 adhering contact with the surface. If the top 30
 surface of layer 26 is essentially tack-free, the
 fabric 30 may not adhere to the surface, while
 if layer 26 has been insufficiently gelled, a
 porous cotton fabric, when used as sheet 30,
 might wick up a portion of the plastisol or 35
 plasticiser in layer 26 and become discoloured.

The laminate formed from backing sheet 12,
 gel layer 18, gel layer 26, and backing sheet
 30 is then heated in oven 34 to a temperature
 sufficient to decompose the blowing agent in 40
 layers 18 and 26 to create two blown cellular
 layers 32 and 33 which layers are bonded
 together by a surface of tensile discontinuity

35. Typically, the laminate should be heated to a temperature of from about 375° to 435°F. until substantially all blowing agent has decomposed.

- 5 The cellular laminate emerging from oven 34 is then delaminated by stripping the backing sheet 30 with cellular layer 32 from cellular layer 33 and the backing sheet 12. The stripping operation may be accomplished by 10 a rapid or gradual pulling apart of the respective coated sheet materials. In the process described, the stripping is carried out just after the cellular laminate emerges from oven 34 so that the temperature of stripping is 15 approximately 275° to 350°F. Of course, if desired, the laminate may be stored as the gelled laminate or as the cellular laminate and the stripping operation carried out when required. As the backing sheet 30 is pulled in 20 one direction and the backing sheet 12 in another, the laminate will delaminate along the general planar surface of contact between layers 33 and 32 where there is a tensile gradient or tensile discontinuity between the resin layers created by the formulations used. 25 The greater hot strength of the layer 32 will create a natural suede-like ruptured cell surface on the cellular layer 32 while the surface of cellular layer 33 may be more grainy in nature. 30

Figure 2 shows representative cross-sectional views of the backing sheet 12, layers 18 and 26, backing sheet 30, and cellular layers 32 and 33 as the materials pass through the corresponding steps of Figure 1. Figures 2g and h illustrate the irregular surfaces 40 and 42 as prepared by the controlled stripping which surfaces have a suede-like appearance.

- The two backing sheets may be made of 40 the same or different materials. For example, woven and non-woven natural and synthetic sheet materials may be employed as desired, such as woven sheet materials like cotton, wool and silk, hemp, felt, or knitted materials 45 or fabrics which are extensible and stretchable in one or more directions. Fibrous materials which may be used to prepare the backing sheets include glass fibres, kraft paper, rayon, nylon, polyethylene, polypropylene, urethane, 50 acrylics or other synthetic fibrous material such as polyesters or combinations thereof. The backing sheets may be smooth sheet materials, or may be embossed with, for example, a decorative design, to impart a decorative 55 suede-like surface appearance. Further, the backing sheet material may have one or more other coatings thereon such as primer or bonding or decorative coatings. In the process illustrated in Figure 1, the cellular-coated backing sheet 38 which has only a thin cellular layer thereon may be re-used several 60 times as the backing sheet 12 in the process or, if desired, it may be employed for covering or decorative or other purposes where a suede-like or roughened finish is desirable. 65

Figure 3 illustrates an alternative embodiment of the method of the invention which employs calendered vinyl chloride resin sheet materials as the intermediate layers of the laminate. Suitable such calendered sheet materials are described in U.S. Patent Specification No. 2,964,799. As shown in Figure 3 a thin calendered polyvinyl chloride sheet 50 containing a blowing agent is unrolled and one surface heated, for example by infrared 75 heaters 52, to a soft condition, but insufficiently to decompose the blowing agent therein. The tacky surface of sheet 50 is then brought into contact with the surface of a backing sheet 54 of any suitable fabric to 80 adhere thereto after passing through a pair of contacting rollers. Another polyvinyl chloride calendered sheet 58 formulated as in Table II also has one surface heated to a tacky condition by infrared heaters 56 which surface is 85 then pressed against the upper surface of calender sheet 50 through calender rolls. Of course if desired, the upper surface of sheet 50 could be treated or both contacting surfaces heated prior to bonding of sheets 50 and 58. 90

Sheet 58 may be a calendered laminate comprising a backing sheet having secured thereto a calendered sheet of a vinyl chloride resin containing a blowing agent or, as illustrated in Figure 3, a separate backing sheet 61 of any suitable fabric may be passed into contact with the top surface of the calendered vinyl chloride resin sheet 58 after rendering the surface tacky through heaters 59. The bonded laminate of backing sheet 61, calendered sheet 58, calendered sheet 50 and backing sheet 54 is then passed to an oven 60 wherein the bonded laminate is heated to a temperature 105 of about 400° to 425°F. to decompose the blowing agents in both resin layers 50 and 58 to create blown or cellular layers 62 and 64 respectively. Upon emergence from the oven at a temperature of about 340° to 360°F. the backing sheet 61 with layer 64 is stripped 110 away across substantially the surface plane of contact between layers 62 and 64 from backing sheet 54 and cellular layer 62 to provide two separate cellular coated fabrics each having a suede-like cellular surface finish. 115

Figure 4 is a cross-sectional representation of the suede-like materials prepared by the calender method illustrated by Figure 3 wherein the suede-like surfaces 66 and 68 are similar in nature. In this illustration the calendered sheets are approximately equal in thickness, but as before of different resin strength so that, at the stripping temperature used, there is created a tensile gradient across the surface of bonding thereby permitting the controlled stripping. However, in this case two separate products are obtained, one having a mirror image suede-like finish relative to the other. 125

Figures 5 and 6 are photographic reproductions 130

tions enlarged 10 times of the surface of a sample of a suede-like material prepared by the plastisol method illustrated by Figure 1. The photographs were taken with a "Hasselblad" (Registered Trade Mark) with a 150 mm lens and a Plus 3 close-up attachment. A 300 watt condenser light source was employed. The film was "KODAK" (Registered Trade Mark) TRI-X Film, ASA 400. Normal development in D-76 was employed.

In Figure 5 the camera and light source were positioned on opposite sides of the sample at 45° angles to the plane of the material. That is, the axis of the camera and axis of the light source made a 90° angle. Exposure was for 250th of a second at F32.

In Figure 6, the camera was at an angle of 90° to the plane of the sample and the light source was at an angle of 5°. Exposure was for 125th of a second at F32.

The invention has been illustrated with particular resin formulations. However, as set forth in U.S. Patent Specifications Nos. 2,964,799 and 3,041,193, various thermoplastic resins as well as monomeric and polymeric plasticisers, blowing agents, fillers and other materials may be employed in resin formulations. While the invention has been described wherein both of the intermediate layers have been blowable vinyl chloride resin layers, it should be recognised that both intermediate layers need not be blowable vinyl chloride resin layers, and that a vinyl chloride resin with or without a blowing agent or another thermoplastic resin may be employed as an intermediate layer to provide the controlled stripping and delamination from the cellular intermediate resin layer and to provide the suede-like product. The selection of a resin formulation to employ for an intermediate layer on a backing sheet requires that the resin form a bond with the blowable resin layer from which it is to be later stripped, yet the bond must be such as to be easily stripable therefrom after blowing of the blowable layer essentially along the plane of bonding between the intermediate layers. Various thermoplastic resins may accordingly be used in the intermediate layers with or without blowing agents to provide the suede-like surface materials of this invention.

WHAT WE CLAIM IS:—

1. A method of preparing a sheet material having a suede-like surface appearance which comprises forming a laminate comprising two outer layers forming backing sheets and two intermediate layers of thermoplastic resin, at least one of the intermediate layers having a cellular structure, and stripping apart the two backing sheets along the bonding plane between the two intermediate layers whereby to rupture the cells at the surface of the cellular layer and to impart a suede-like surface appearance to the intermediate layer or layers of cellular structure.

2. A method according to claim 1, wherein the intermediate layer of cellular structure is formed from a blown vinyl chloride resin formulation.

3. A method according to claim 1 or 2, wherein both of the intermediate layers have a cellular structure.

4. A method according to claim 1 or 2, wherein the thickness of any non-cellular intermediate layer is from 1 to 10 mils.

5. A method according to claim 4, wherein the thickness is from 3 to 6 mils.

6. A method according to any of claims 1 to 5, wherein the thickness of each layer of cellular structure is from 5 to 50 mils.

7. A method according to claim 6, wherein the thickness is from 10 to 30 mils.

8. A method according to any of the preceding claims, wherein the relative thicknesses of the two intermediate layers are in the range from 5:1 to 1:5.

9. A method according to claim 1, wherein a first backing sheet is coated with a first intermediate layer from 1 to 10 mils thick of a vinyl chloride plastisol containing a blowing agent;

the first intermediate layer is heated to a temperature sufficient to gel the vinyl chloride resin to a tack-free surface but insufficient to decompose the blowing agent;

a second intermediate layer from 5 to 30 mils thick of a vinyl chloride plastisol containing a blowing agent is coated on the first intermediate layer;

the second intermediate layer is heated to a temperature sufficient to gel the layer but insufficient to decompose the blowing agent therein, and to provide a tacky upper surface to the layer;

a second backing sheet is bonded to the tacky upper surface of the second intermediate layer to form a laminate;

the laminate so formed is heated to a temperature sufficient to decompose the blowing agents in the first and second intermediate layers thereby to provide them with cellular structures; and

the first and second backing sheets are stripped apart, the separation of the laminate taking place substantially along the bonding plane between the first and second intermediate layers, thereby to rupture the cells at the surface of at least one of the intermediate layers and to impart a suede-like surface appearance to one or both of the intermediate layers.

10. A method according to claim 1, wherein a first intermediate layer comprising a calendered polyvinyl chloride sheet containing a blowing agent is heated on one surface to a temperature sufficient to render it tacky but insufficient to decompose the blowing agent;

a first backing sheet is bonded to the tacky surface of the first intermediate layer;

a second intermediate layer comprising a calendered polyvinyl chloride sheet containing

- a blowing agent is heated to a temperature sufficient to render one surface tacky but insufficient to decompose the blowing agent and the tacky surface of the second intermediate layer is contacted with the free surface of the first intermediate layer;
- 5 a second backing sheet is bonded to the tacky free surface of the second intermediate layer to form a laminate;
- 10 the laminate so formed is heated to a temperature sufficient to decompose the blowing agents in the first and second intermediate layers thereby to provide them with cellular structures; and
- 15 the first and second backing sheets are stripped apart, the separation of the laminate taking place substantially along the bonding plane between the first and second intermediate layers, thereby to rupture the cells at the surface of at least one of the intermediate layers and to impart a suede-like surface appearance to one or both of the intermediate layers.
- 20 11. A method according to any of the preceding claims, wherein the temperature of the laminate at the time of stripping apart the backing sheets is from 250 to 450°F.
12. A method according to any of the preceding claims, wherein the compositions from which the intermediate layers are formulated are such as to provide different hot film strengths in the intermediate layers at the temperature of the stripping apart step.
13. A method of preparing sheet materials having a suede-like surface appearance substantially as hereinbefore described with reference to Figures 1 and 3 of the accompanying drawings.
14. A method of preparing sheet materials having a suede-like surface appearance according to claim 1 substantially as hereinbefore described.
15. Sheet materials having a suede-like surface appearance whenever prepared by a method as claimed in any one of claims 1 to 14.
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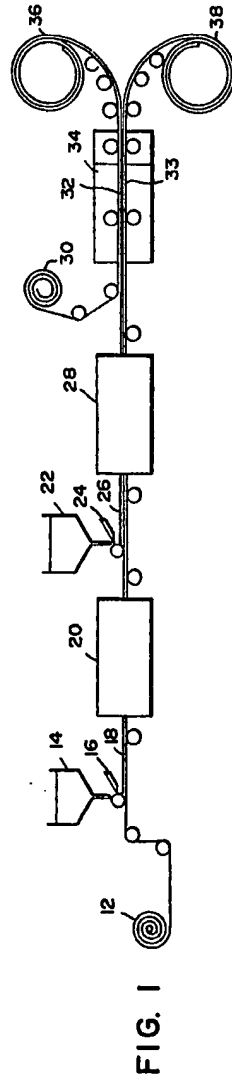


FIG. 1

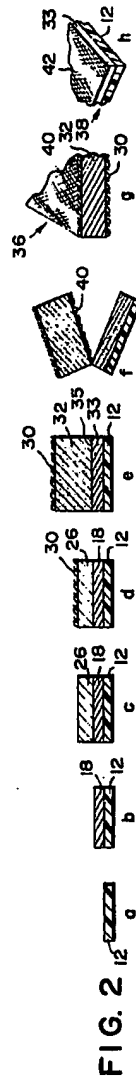


FIG. 2

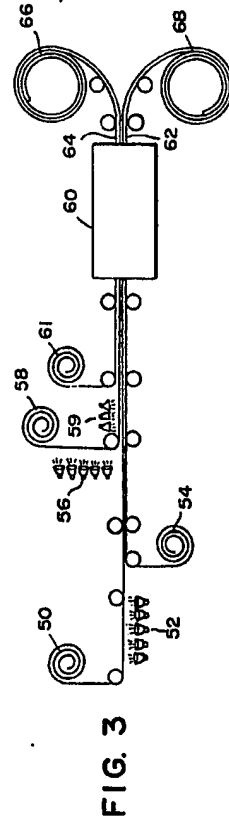


FIG. 3



FIG. 4

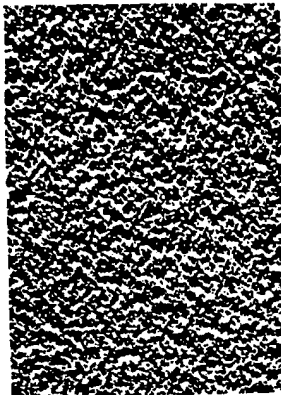


FIG. 5



FIG. 6